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TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

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U.S. APPLICATION NO. (if known)

09/856912

INTERNATIONAL APPLICATION NO.

PCT/DE 00/03384

INTERNATIONAL FILING DATE

September 28, 2000

PRIORITY DATE CLAIMED

September 30, 1999

## TITLE OF THE INVENTION

Method for Operating a Mixed-Potential Exhaust-Gas Probe and Circuit Arrangements for Carrying Out the Methods

## APPLICANT(S) FOR DO/EO/US

Bernd Mueller, Thomas Brinz, Bernd Schumann and Bernhard Bloemer

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is the **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is the **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
  3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
  4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
    - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ has been transmitted by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2))
  7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☐ have not been made and will not be made.
  8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
  10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:**
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment
  14. ☐ A substitute specification.
  15. ☐ A change of power of attorney and/or address letter.
  16. ☒ Other items or information:
    1. Four (4) sheet(s) of drawing.
    2. Form PCT/RO/101
    3. Form PCT/ISA/210
    4. Form PCT/ISA/220

U.S. APPLICATION NO. (if known)

09/856912

INTERNATIONAL APPLICATION NO.  
PCT/DE 00/03384ATTORNEY'S DOCKET NUMBER  
R 3612717. ☒

The following fees are submitted:

**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO ..... \$860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$690.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))..... \$760.00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO..... \$970.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$96.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$860.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

Claims	Number Filed	Number Extra	Rate
Total Claims	8 - 20 =	0	X \$18.00
Independent Claims	4 - 3 =	1	X \$80.00
Multiple dependent claim(s) (if applicable)			+ \$270

**TOTAL OF ABOVE CALCULATIONS =**

\$940.00

Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).

**SUBTOTAL =**

\$940.00

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).**TOTAL NATIONAL FEE =**

\$940.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +**TOTAL FEES ENCLOSED =**

\$940.00

Amount to be  
refunded  
charged

- a. ☒ A check in the amount of \$940.00 to cover the above fee is enclosed.
- b. ☐ Please charge my Deposit Account No. 15-0773 in the amount of \$840.00 to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0773. A duplicate copy of this sheet is enclosed.

**Note:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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On page 1, between lines 22 and 23, please insert the following:

-- Summary of the Invention --.

On page 2, please delete lines 2 to 4.

On page 2, lines 11 and 12, please delete "This task is furthermore solved also with the features of claim 3.".

On page 2, please delete lines 21 to 24.

On page 3, please delete lines 16 to 20 and substitute therefor the following:

-- Brief Description of the Drawings

The invention will now be described with reference to the drawings wherein: --.

On page 4, please delete line 4 and substitute the following:

-- Description of the Preferred Embodiments of the Invention --.

In the Abstract:

On page 11, please delete line 1 and substitute therefor:

-- Abstract of the Disclosure --.

In the Claims:

Please cancel claims 1 to 7 and add claims 8 to 15 as follows:

8. A method for operating a mixed-potential exhaust-gas probe for an internal combustion engine, the exhaust-gas probe including: a heatable probe ceramic; a first electrode arranged in a chamber subjected to a reference atmosphere; and, a second  
5 electrode, which detects gas molecules, and is arranged in the exhaust gas of the internal combustion engine; the method comprising the steps of:

providing a pump voltage source and applying a pump voltage across the first and second electrodes so that, in the interior  
10 of the chamber, a somewhat reduced oxygen partial pressure is adjusted by the electrochemical pumping off of the oxygen molecules;

applying a constant external voltage to the electrodes with this voltage deviating from the thermodynamic equilibrium voltage  
15 of the wanted reaction; and,

measuring and evaluating the current dropping across the electrodes.

9. The method of claim 8, comprising the further step of experimentally determining the optimal voltage for detecting individual mixed potentials of individual components of the exhaust gas.

10. A method for operating a mixed-potential exhaust-gas probe for an internal combustion engine, the exhaust-gas probe including: a heatable probe ceramic detecting gas molecules; a first electrode mounted in a chamber and the first electrode  
5 being subjected to a reference atmosphere; and, a second electrode arranged in the exhaust gas of the internal combustion engine; the method comprising the steps of:

providing a pump voltage source and applying a pump voltage across the first and second electrodes so that a somewhat reduced  
10 oxygen partial pressure is adjusted in the interior of the chamber by electrochemically pumping off the oxygen molecules; and,

applying a constant current to the probe ceramic and measuring and evaluating the voltage adjusting between the first  
15 and second electrodes with this voltage deviating from the thermodynamic equilibrium voltage of the desired reaction.

11. The method of claim 10, comprising the further step of experimentally determining the current for detecting individual mixed potentials of individual components of the exhaust gas.

12. A circuit arrangement for carrying out a method for operating a mixed-potential exhaust-gas probe for an internal combustion engine, the exhaust-gas probe including: a heatable probe ceramic; a first electrode arranged in a chamber subjected  
5 to a reference atmosphere; and, a second electrode, which detects gas molecules, and is arranged in the exhaust gas of the internal combustion engine; the method comprising the steps of: providing

a pump voltage source and applying a pump voltage across the first and second electrodes so that, in the interior of the chamber, a somewhat reduced oxygen partial pressure is adjusted by the electrochemical pumping off of the oxygen molecules; applying a constant external voltage to the electrodes with this voltage deviating from the thermodynamic equilibrium voltage of the wanted reaction; and, measuring and evaluating the current dropping across the electrodes; the arrangement comprising:

- an inverting operational amplifier having a non-inverting input, an inverting input and a feedback loop;
- a voltage divider R2 connected to said non-inverting input; the exhaust-gas probe being connected to said inverting input;
- a reference resistor R1 arranged in said feedback loop; and,
- a difference amplifier which amplifies the voltage difference between said non-inverting input and the output of the operational amplifier and outputs the difference as a measurement signal.

13. The circuit arrangement of claim 12, further comprising a switching device for switching the circuit arrangement for the voltage polarized current measurement over to the circuit arrangement for current polarized voltage measurement.

14. A circuit arrangement for carrying out a method for operating a mixed-potential exhaust-gas probe for an internal combustion engine, the exhaust-gas probe including: a heatable probe ceramic detecting gas molecules; a first electrode mounted

5 in a chamber and the first electrode being subjected to a  
reference atmosphere; and, a second electrode arranged in the  
exhaust gas of the internal combustion engine; the method  
including the steps of: providing a pump voltage source and  
applying a pump voltage across the first and second electrodes so  
10 that a somewhat reduced oxygen partial pressure is adjusted in  
the interior of the chamber by electrochemically pumping off the  
oxygen molecules; and, applying a constant current to the probe  
ceramic and measuring and evaluating the voltage adjusting  
between the first and second electrodes with this voltage  
15 deviating from the thermodynamic equilibrium voltage of the  
desired reaction; the arrangement comprising:

a non-inverting operational amplifier having a non-inverting  
input, an inverting input and a feedback loop;

a voltage divider R2 connected to the non-inverting input;

20 a reference resistor R1 connected to the inverting input;

said exhaust-gas probe being arranged in said feedback loop; and,

a difference amplifier for amplifying the voltage difference  
at the sensor and outputting said voltage difference as a  
measurement signal.

15. The circuit arrangement of claim 14, further comprising a  
switching device for switching the circuit arrangement for the  
voltage polarized current measurement over to the circuit  
arrangement for current polarized voltage measurement.



Remarks

Claims 8 to 15 have been added and claims 1 to 7 are cancelled so that claims 8 to 15 are pending in this application of which claims 8, 10, 12 and 14 are in independent form. The new claims make improvements as to the form of the original claims.

The disclosure has been amended to add appropriate headings and to make needed corrections.

Respectfully submitted,



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JG12 Rec'd PCT/PTO 3 0 MAY 2001

Attorney Docket No: R 36127

Methods for Operating a Mixed-Potential Exhaust-Gas Probe and  
Circuit Arrangements for Carrying Out the Methods  
State of the Art

5           The invention relates to methods for operating a  
mixed-potential exhaust-gas probe and circuit arrangements for  
carrying out these methods in accordance with the preamble of the  
independent claims 1, 3, 5 and 6.

10           Mixed-potential exhaust-gas probes are utilized, for  
example, as gas sensors to detect the hydrocarbon concentration  
of the internal combustion engine or as NOx probes for detecting  
the nitrogen oxide component in the exhaust gas of internal  
combustion engines.

15           These probes are with respect to their configuration similar  
to the  $\lambda$ -probes and are presented, for example, in the text of  
Bosch entitled "Kraftfahrtechnisches Taschenbuch", 22nd edition,  
1995, starting at page 490.

20           In known mixed-potential exhaust-gas probes, the signal is  
measured: as a voltage between two electrodes; via the  
short-circuit current between the electrodes; or, by tapping the  
voltage measurable between the electrodes and dropping across a  
resistor.

25           It is an object of the invention to provide a method for  
operating a mixed-potential exhaust-gas probe wherein a highest  
possible selectivity is made possible with respect to the  
individual components of the exhaust gas even in the presence of  
sometimes very large transverse sensitivities.

30           Furthermore, it is an object of the invention to provide  
circuit arrangements which make possible to carry out the methods  
with a technically simple configuration and the least number of

components.

# Advantages of the Invention

The first mentioned task is solved by the features of claim 1.

5 By applying a constant external voltage, the probe can be adjusted to some extent to individual exhaust-gas constituents which are to be detected. The external voltage is different from the thermodynamic equilibrium voltage.

10 The external constant voltage is determined previously and preferably experimentally.

This task is furthermore solved also with the features of claim 3. In this case too, the exhaust-gas probe is adjusted to a certain extent to the detection of individual gas components of the exhaust gas.

15 The magnitude of the current, which is to be applied to the probe ceramic, is determined experimentally.

The sensitivity of the probe can be considerably increased by the voltage or the current which is distinguished from the thermodynamic equilibrium voltage and the thermodynamic equilibrium current, respectively.

20 The last-mentioned task according to the invention is further solved by circuit arrangements having the features of claims 5 and 6.

A voltage-polarized current measurement (that is, a measurement of the current which drops on the electrodes of the mixed-potential exhaust-gas probe) at constant external voltage can be realized in a technically very simple manner with an inverting operational amplifier. A voltage divider is connected to the non-inverting input of the operational amplifier and one of the electrodes of the exhaust-gas probes is connected to the



FIG. 5 shows an embodiment of a circuit arrangement according to the invention for the current-polarized voltage measurement.

#### Description of the Embodiments

5           FIG. 1 shows, in section, an exhaust-gas probe 1.2 on an exhaust-gas pipe of which a wall 1.1 is shown. This wall 1.1 partitions the exhaust gas of an internal combustion engine (left) from the ambient air (right). The exhaust-gas probe 1.2 includes a solid-state electrolyte 1.3 in its exhaust-gas end  
10           portion. The solid-state electrolyte 1.3 is between a first electrode 1.4 subjected to the exhaust gas and a further electrode 1.5. A reference gas volume 1.6 communicates with the electrode 1.5 and is in direct contact with the ambient air via a channel 1.9. The electrode 1.5 is connected to a measuring  
15           feedline 1.10 and the electrode 1.4 is connected to a measurement line 1.11.

          For maintaining a stable reference atmosphere, it is essential that the supply of oxygen via the pump current  $I_p$  exceeds, in time average, the occurring losses of oxygen. Such  
20           losses occur perforce during the measurement of a voltage in the electrodes when the voltage measurement is based on a current measurement via a measuring resistor in a manner known per se. Typically, measurement resistors in the megaohm range are used in the range of the measurement of voltages in the order of  
25           magnitude of the output voltage of the exhaust-gas probe of 1 V. As a consequence, a measurement current flows in the microampere range. For electrolytes, this current is carried by oxygen ions from the reference volume so that the oxygen concentration in the reference gas volume reduces because of the measurement.

30           A measurement pulse can be so dimensioned with respect to

its height and time duration that it supplies the required pump current in time average.

The basic idea of the invention is to achieve an improvement of the gas selectivity in that a constant external potential or a constant external current is applied to the sensor electrodes (1.4, 1.5). In this way, the signal formation can be adjusted to a certain extent to individual gases and thereby the selectivity can be improved. If a constant external potential, that is, a constant external voltage is applied, which deviates from the thermodynamic equilibrium voltage, the adjusting current is measured and evaluated. If a constant current is applied, then the measurement and evaluation of the potential, which adjusts, or the voltage, which adjusts, takes place.

By applying a voltage which lies above the thermodynamic equilibrium voltage of the disturbing electrode reaction, it is especially possible to influence the course of the disturbing reaction so that no disturbing components participate in the wanted reaction.

FIG. 4 shows an embodiment of a circuit arrangement for the voltage-polarized current measurement wherein one applies a constant external voltage to the electrodes (1.4, 1.5) of the exhaust-gas probe and measures and evaluates the current dropping via the electrodes (1.4, 1.5). The applied voltage deviates from the thermodynamic equilibrium voltage. The circuit includes an operational amplifier having a feedback loop in which a reference resistance R1 is connected; that is, the reference resistance R1 is connected between the inverting input of the operational amplifier and the output thereof. The exhaust-gas probe is connected to ground at the inverting input. A voltage divider identified by R2 is connected to the non-inverting input of the

operational amplifier. A differential amplifier is arranged between the non-inverting input and the output and the output signal to ground is the measurement signal. If the internal resistance or the potential at the exhaust-gas probe changes, then the operational amplifier controls the voltage, which is present at the exhaust-gas probe, via the reference resistance R1 which acts as a feedback resistor. The signal between the non-inverting input and the output of the operational amplifier is proportional to the current which flows through the sensor and is amplified by the differential amplifier.

The circuit further includes a three-way switch S1 by means of which switching can take place to the circuit arrangement shown in FIG. 5. The circuit arrangement shown in FIG. 5 defines a current-polarized voltage measurement wherein a constant current can be applied to the probe ceramic and the voltage which adjusts can be measured and evaluated. The circuit arrangement shown in FIG. 5 distinguishes from the circuit arrangement in FIG. 4 in that the reference resistor R1 is connected to the inverting input of the operational amplifier; in contrast, the exhaust-gas probe is arranged in the feedback loop of the operational amplifier. The voltage divider R2 is connected to the non-inverting input. In this case, the differential amplifier amplifies the voltage dropping across the exhaust-gas probe and this voltage is evaluated as a measurement signal. In this circuit, a current is impressed upon the exhaust-gas probe and this current is determined only by the voltage adjusted via the voltage divider (that is, by means of the potentiometer R2) and the resistor R1. Since the exhaust-gas probe lies in the feedback of the operational amplifier, the internal resistance of the exhaust-gas probe has no influence on the impressed current.

The voltage drop across the exhaust-gas probe is measured with the aid of the differential amplifier.

As an example, FIG. 2 shows the mixed potentials of hydrocarbons (450-45 ppm) (reference numeral 1) as well as the mixed potentials of nitrogen oxides (reference numeral 2). These mixed potentials are detected by means of a voltage-polarized current measurement (see FIG. 4) for a polarization voltage of +290 mV.

If the electrode is negatively polarized, then the signal amplitude of the hydrocarbon mixed-potential formations drops with increasing negative polarization (reference numeral 1a). The nitrogen oxide signal first drops with falling polarization voltage, reverses and then increases with increasing negative polarization voltage to 100 mV for a polarization voltage of -500 mV (reference numeral 2a).

In FIG. 3, the amplitude of the hydrocarbon mixed-potential formations (transverse sensitivity) is plotted against the pump voltage or polarization voltage.

As shown in FIG. 3, no hydrocarbon transverse sensitivity is present for a pump voltage of -600 mV so that a measurement is possible of only the NOx component.



Patent Claims

1. Method for operating a mixed-potential exhaust-gas probe for an internal combustion engine having a heatable probe ceramic 1.3 with a first electrode 1.5, which is arranged in a chamber 1.6 and is subjected to the reference atmosphere and with a second  
5 electrode 1.4 which detects gas molecules and is arranged in the exhaust gas of the internal combustion engine, a pump voltage being applied between the first and second electrodes by means of a pump voltage source, so that, in the interior of the chamber 1.6, a somewhat reduced oxygen partial pressure is  
10 adjusted by the electrochemical pumping off of the oxygen molecules, characterized in that one applies a constant external voltage to the electrodes (1.4, 1.5) with this voltage deviating from the thermodynamic equilibrium voltage of the wanted reaction, measuring and evaluating the current dropping across  
15 the electrodes (1.4, 1.5).

2. Method of claim 1, characterized in that one determines the optimal voltage for detecting individual mixed potentials of individual components of the exhaust gas experimentally.

3. Method for operating a mixed-potential exhaust-gas probe for an internal combustion engine having a heatable probe ceramic 1.3 detecting gas molecules and having a first electrode 1.5 mounted in a chamber 1.6, the first electrode 1.5 being subjected to the reference atmosphere, and having a second electrode arranged in the exhaust gas of the internal combustion engine, wherein a pump voltage is applied between the first and second electrodes 1.4 with a pump voltage source so that a somewhat reduced oxygen

partial pressure is adjusted in the interior of the chamber 1.6 by electrochemically pumping off the oxygen molecules, characterized in that one applies a constant current to the probe ceramic and measures and evaluates the voltage adjusting between the electrodes (1.4, 1.5) with this voltage deviating from the thermodynamic equilibrium voltage of the desired reaction.

4. Method of claim 3, characterized in that one determines the current for detecting individual mixed potentials of individual components of the exhaust gas experimentally.

5. Circuit arrangement for carrying out the method of claim 1 or 2, characterized by an inverting operational amplifier, with a voltage divider R2 being connected to the non-inverting input of the operational amplifier and the exhaust-gas probe being connected to the inverting input of the operational amplifier and a reference resistor R1 being arranged in the feedback loop; and, a differential amplifier which amplifies the voltage difference between the non-inverting input and the output of the operational amplifier and outputs the difference as a measurement signal (voltage polarized current measurement, FIG. 4).

6. Circuit arrangement for carrying out the method of claim 3 or 4, characterized by a non-inverting operational amplifier having a non-inverting input and an inverting input, a voltage divider R2 being connected to the non-inverting input and a reference resistor R1 being connected to the inverting input, an exhaust-gas probe being arranged in the feedback loop of the operational amplifier and having a differential amplifier which amplifies the voltage difference at the sensor and outputs this

voltage difference as the measurement signal (current polarized voltage measurement, FIG. 5).

7. Circuit arrangement of claim 5 or 6, characterized in that a switching device is provided via which the circuit arrangement for the voltage polarized current measurement can be switched over to the circuit arrangement for current polarized voltage measurement.



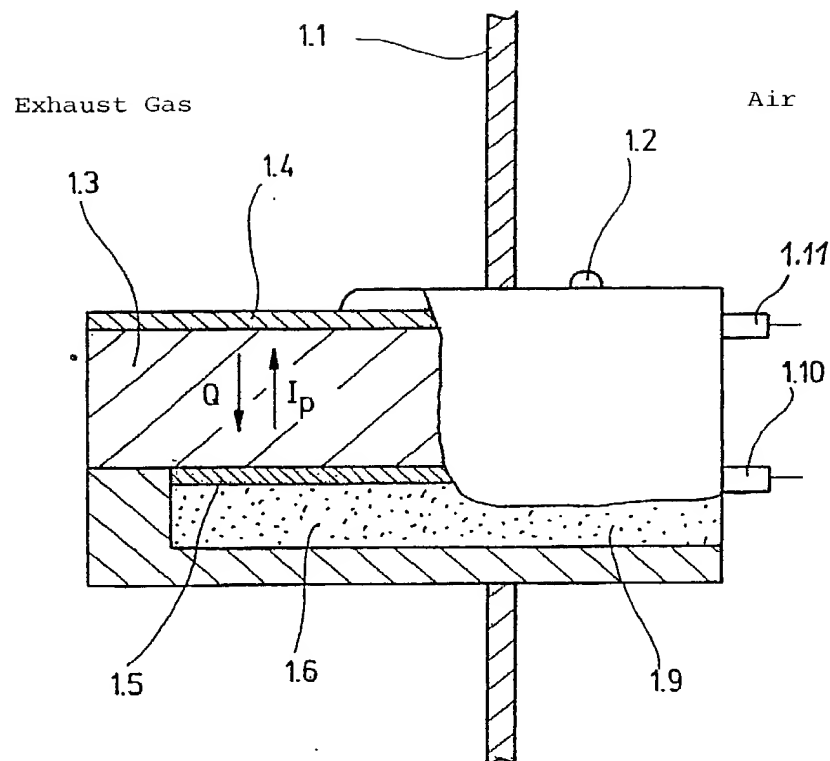


Fig.1

(State of the Art)

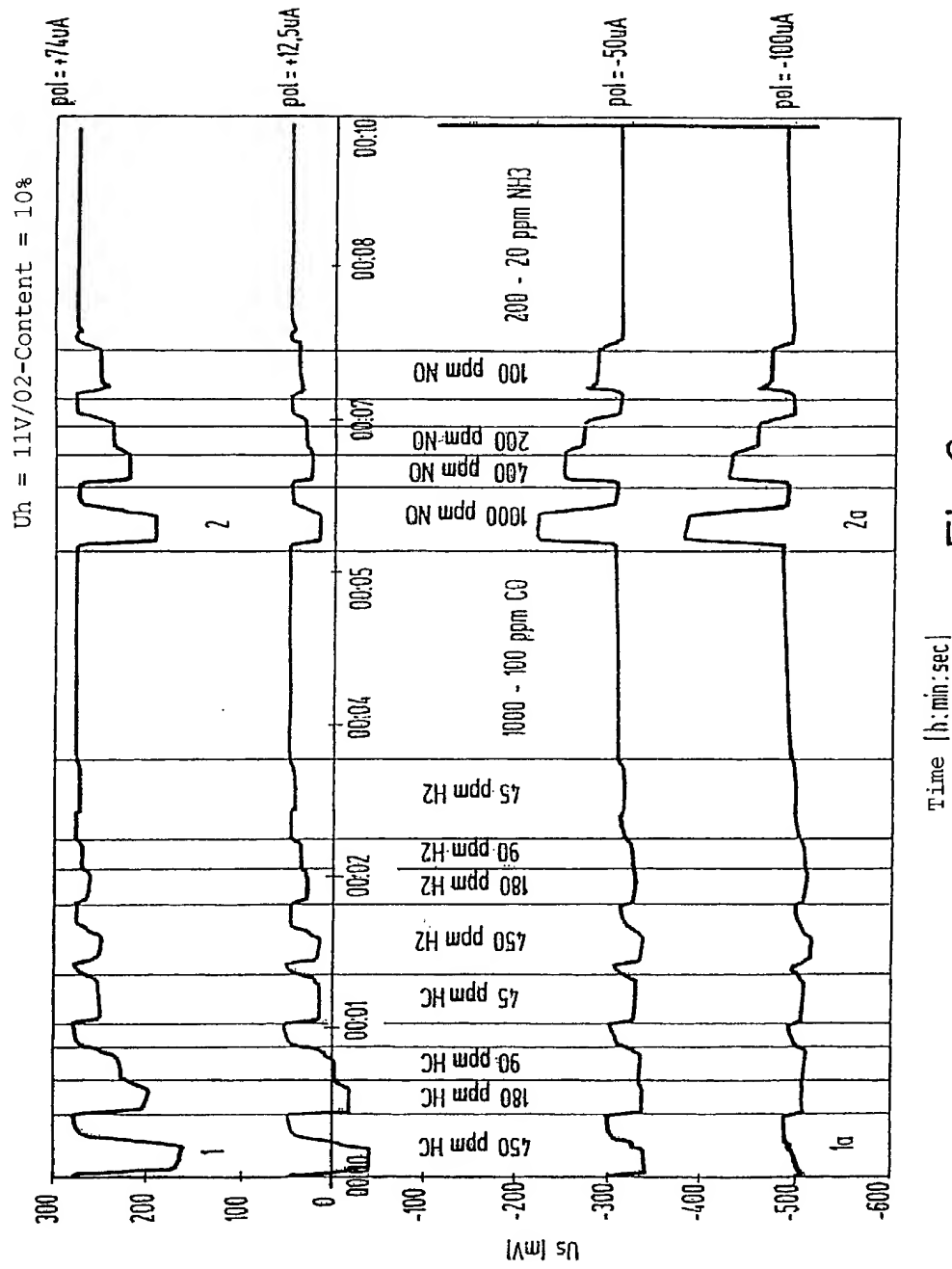


Fig.2

Dependency of the HC Transvers Sensitivity of a  
NOx-Mixed Potential Sensor on the Polarization Voltage

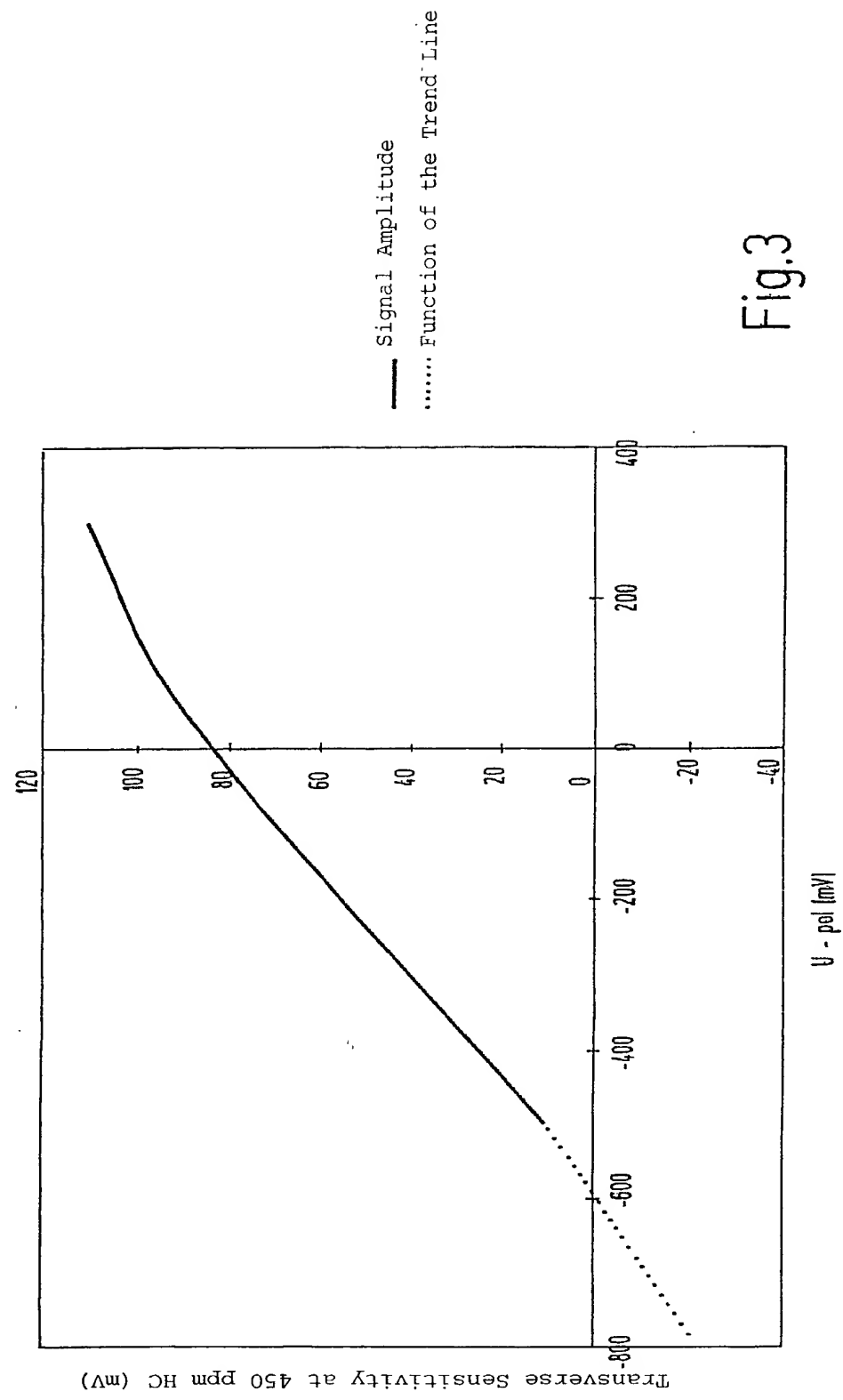


Fig.3

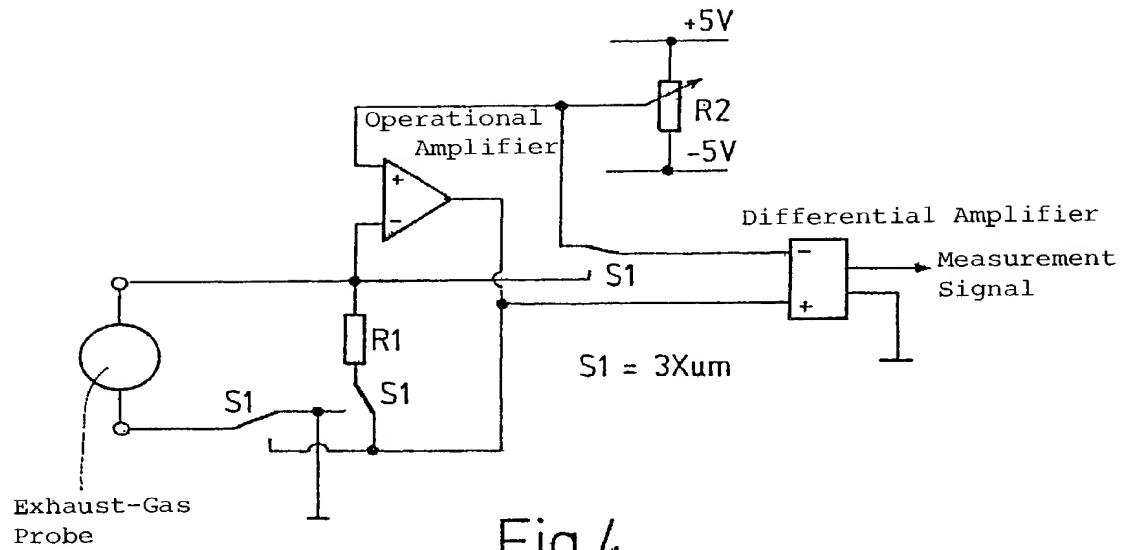


Fig.4

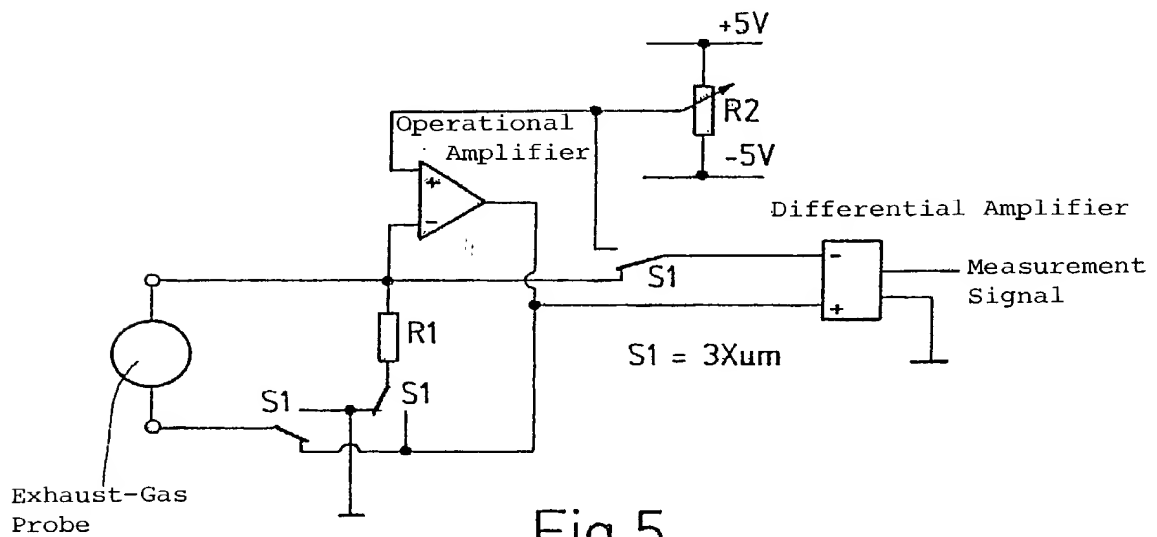


Fig.5



Declaration and Power of Attorney for National Stage of PCT Patent Application

As a below named inventor, I hereby declare that: .

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: Methods for Operating a Mixed-Potential Exhaust-Gas Probe and Circuit Arrangements for Carrying Out the Methods, the specification of which was filed as PCT International Application Number PCT/DE 00/03384 on September 28, 2000.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119, of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

<u>Prior Foreign Application(s)</u>			<u>Priority Claimed</u>	
<u>199 47 240.8</u> (Number)	<u>Federal Republic of Germany</u> (Country)	<u>30 Sep 99</u> Date Filed	<u>X</u> Yes	<u>      </u> No
<u>      </u> (Number)	<u>      </u> (Country)	<u>      </u> Date Filed	<u>      </u> Yes	<u>      </u> No

As a named inventor, I hereby appoint the following attorney to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor, if any Bernd Mueller

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